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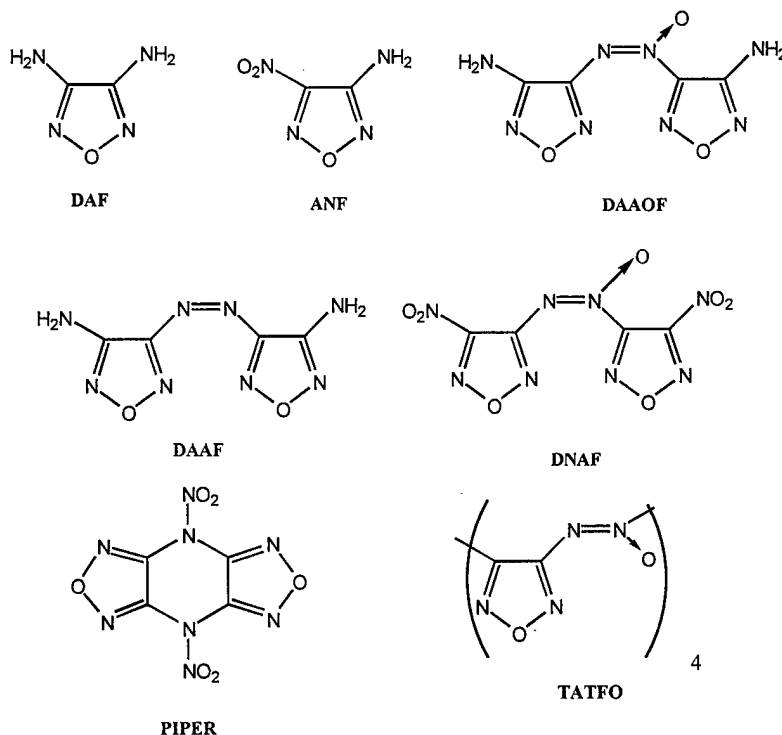
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Furazan-Based Energetic Ingredients

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ABSTRACT

A series of furazan-based energetic materials derived from 3,4-diaminofurazan (DAF) were synthesized and characterized. These compounds included diaminoazoxyfurazan (DAAOF), diaminoazofurazan (DAAF), dinitroazoxyfurazan (DNAF), aminonitrofurazan (ANF), dinitrobisfurazanopyrazine (PIPER), and tetrazoxytetrafurazan (TATFO). Characterization testing included small scale safety testing (impact, friction, ESD, thermal stability), DSC analysis, vacuum thermal stability (VTS), and ingredient compatibility (by DSC). Results from these tests indicated that most of the materials have excellent thermal stability, as determined by DSC analysis. However, the small scale safety properties and ingredient compatibilities of most of these materials with standard propellant ingredients were found to be unsuitable for an acceptable propellant ingredient. The most promising furazan-based material investigated was DAAOF, based upon the above criteria.



INTRODUCTION

Energetic compounds which contain nitrate ester and nitramine functional groups are inherently fairly sensitive to impact, friction and ESD stimuli due to the presence of these energetic moieties. However, other heteroatomic structures such as furazan, azoxy, azo and C-nitro groups can be used to construct energetic compounds without the higher sensitivities noted above. Several of these materials are already known or in development. In particular, a series of compounds based upon the furazan structure have been investigated during the last few years at Thiokol. Much has been learned about the effects of different chemical groups attached to the furazan ring in terms of thermal stability, small scale safety properties, and ingredient compatibility of the resulting substituted furazan-based ingredients. The data obtained from past efforts will be presented along with current research results from several programs.

RESULTS AND DISCUSSION

The common precursor to DAAOF, DAAF, DNAF, ANF, and PIPER is DAF. A two step procedure recently reported in the literature¹ was modified in order to multi-hundred gram quantities of material (see Figure 1). The first step involved the synthesis diaminoglyoxime (DAG) from aqueous glyoxal and excess hydroxylamine. The synthesis of DAG was reported in moderate (52%) yield on a 50-gram scale.¹ The literature procedure was scaled up in the kilo lab. The procedure was modified due to the strong exotherm which occurs at 90-100°C during the reaction. The modification involved the drop-wise addition of glyoxal to a solution of free hydroxylamine at 90°C. If the reaction temperature climbs significantly above this temperature, lower yields of product are obtained. The literature procedure involved the combination of both materials at 10°C, followed by heating of the resulting mixture to reflux. At the 1-kilogram level of isolated product, the yield was increased to 64%. The second step involves the dehydration of DAG at elevated temperature with aqueous caustic in an autoclave. On a 300-gram scale of starting material, 30-47% isolated yields of DAF were obtained.

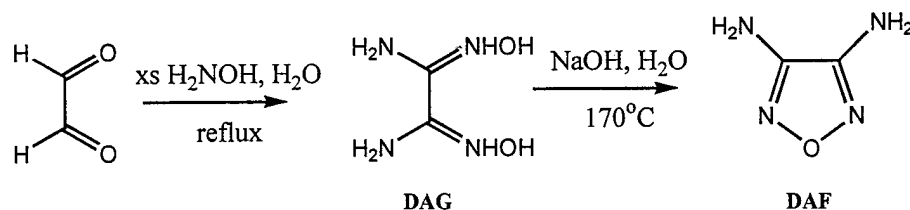


Figure 1. Two Step Synthesis of DAF

DAF can be oxidized with hydrogen peroxide in concentrated sulfuric acid to give the corresponding azoxy compound DAAOF in 90% isolated yield as was first reported by Solodyuk, *et al.* in 1981.² The reaction was reported on a 2-gram scale. However, much larger quantities were needed for the efforts at Thiokol. Therefore, the synthesis was scaled up and the reaction conditions varied in a series of experiments in order to determine the effects on yield and purity of the product. The results are presented in Table 1. Based upon the results, the yield and purity of the final product appeared to be fairly insensitive to the scale and reaction conditions employed. Carbon NMR analysis of the samples obtained indicated that small amounts of impurities (< 5%) were present in the samples. Further purification by recrystallization from

acetonitrile afforded very clean product by carbon NMR analysis. This purified material was submitted for X-ray structure analysis. A report on the structure obtained is available.³

Table 1. Scale Up and Process Variable Studies on the Synthesis of the DAAOF

Experiment	Scale (g)	Conditions	Yield (%)	%C/%H/%N
LH 1422-87	20	30% H ₂ O ₂ (baseline)	90%	22.33/1.96/52.57
LH 1422-88	50	30% H ₂ O ₂ (baseline)	92%	22.40/1.92/52.56
LH 1422-89	50	35% H ₂ O ₂	92%	22.43/1.88/52.68
LH 1422-90	50	35% H ₂ O ₂	88%	22.42/1.89/52.77
LH 1422-97	100	35% H ₂ O ₂	89%	22.31/1.86/53.20
LH 1422-98	50	35% H ₂ O ₂ , fast acid addition	88%	22.33/1.81/53.18
LH 1422-99	50	35% H ₂ O ₂ , 40°C initial exotherm	90%	22.29/1.86/53.32
LH 1469-2	40	20% excess of H ₂ O ₂ , H ₂ SO ₄	90%	22.31/1.83/52.76
LH 1469-3	60	20% deficiency of H ₂ O ₂ , H ₂ SO ₄	90%	22.29/1.86/53.32
Theoretical	N/A	N/A	N/A	22.64/1.89/52.83

Baseline conditions are 30% hydrogen peroxide (H₂O₂), slow sulfuric acid (H₂SO₄) addition (1 hour), and maintaining the initial exotherm below 30°C.

Purified samples of DAAOF were submitted to a number of safety, chemical, and physical tests to completely characterize the material. The data are presented in Table 2. The safety testing indicates that the material is very insensitive for an energetic material. Good thermal stability is indicated by the SBAT, vacuum thermal stability (VTS) test, and DSC results. Particle size analysis results for a typical batch indicated a monomodal distribution with a 55-micron average size. Samples of DAAOF were also submitted for DSC compatibility testing with four propellant ingredients which may be used with this material. These results are presented in Table 3. Based upon the changes in the onset and peak temperatures observed, the results indicate that DAAOF is compatible with GAP-P and TEGDN. In addition, a slight incompatibility with ADN and BTTN may exist. Further testing and small-scale formulation work will better define these initial compatibility results.

Another compound very similar to DAAOF is DAAF. This analog (replacing the azoxy group with an azo group) is produced in 49% yield by the oxidation of DAF with ammonium persulfate in water.⁴ This reaction was scaled to the 100 gram level of starting material, giving 52-67% yields of crude product. Carbon NMR analysis of the crude products indicated that they were mixtures of DAAF and DAAOF (61-64 mole % DAAF). Utilization of longer reaction times at 70°C increased the level of DAAF to 68-69 mole %. In contrast, lowering the amount of excess ammonium persulfate employed by 10-20% gave lower percentages of DAAF (54-60 mole %) in the crude product. A significantly higher yield of crude DAAF (82% yield; 67 mole % DAAF) was obtained when sodium persulfate was used in place of ammonium persulfate. In order to obtain pure samples of DAAF, two different methods of purification were tested. In the first, samples of crude product were boiled in water which dissolved mostly the DAAOF, giving samples which contained 81 mole% DAAF. A second better method was to use soxhlet extraction with tetrahydrofuran (THF), which after evaporation of the filtrate yielded pure samples of DAAF. These purified samples of DAAF were submitted for safety testing and characterization (see Table 4). As was observed for DAAOF, DAAF exhibited low sensitivity and good thermal stability. However, DAAF gave over 5 ml of gas per gram in the VTS test (100°C, 48 hours). This is unacceptable for a propellant ingredient and would have to be remedied if DAAF is to be a viable material.

Table 2. Safety Testing and Characterization of DAAOF

Test	Result
Safety Testing	
ABL impact (cm) – TIL	>80
ABL friction (psi) – TIL	800 @8 ft/s
TC ESD (joules) – 50%	2.4
TC confined ESD (j)	8
SBAT onset (°F)	382
TC impact (inches) - 50%	>46
TC friction (lbs) - 50%	>64
Russian DDT	no go @ 500 psi
IHE card gap (0 cards)	no go
Characterization	
Particle size (micron) – 10%, 50%, 90%	24, 53, 88
DSC onset (°C) – 20°C/min	250-260
VTS (ml of gas/gm) - 100°C, 48 hrs	0.69
H _c (cal/g)	2,891
ΔH _f (kcal/mol; calc)	+100.8
Density (g/ml)	1.7426

For safety testing, the Allegheny Ballistics Laboratory (ABL) tests were threshold initiation levels (TIL) (1 out of 20 GO's). The Thiokol Corporation (TC) tests are 50% values. The electrostatic discharge (ESD) values were measured on a TC-designed instrument and are 50% levels. Simulated bulk autoignition test (SBAT) thermal onsets were determined on two gram samples which were heated at a rate of 24°F/hr. The Russian deflagration to detonation transition (DDT) test and IHE card gap test were performed according to standard procedures. Differential scanning calorimetry (DSC) testing was performed at 20°C/min. The heat of combustion (H_c) was determined by standard methods using a Parr stainless steel bomb under oxygen. Heat of formation (ΔH_f) values were calculated by standard methods, using the measured H_c values. The bulk density was determined by gas pycnometry.

Table 3. DSC Compatibility Testing of DAAOF

Compound	Onset temp (°C)	ΔOnset (°C)	Peak (°C)	ΔPeak (°C)
DAAOF	252	N/A	275	N/A
TEGDN	206	N/A	231	N/A
ADN	182	N/A	205	N/A
BTTN	203	N/A	226	N/A
GAP-p	243	N/A	272	N/A
DAAOF/TEGDN	204	2	225	6
DAAOF/ADN	158	24	208	-3
DAAOF/BTTN	182	19	200	26
DAAOF/GAP-P	230	13	248	26

Table 4. Safety Testing and Characterization of DAAF

Test	Result
Safety Testing	
ABL impact (cm) - TIL	80
ABL friction (psi) - TIL	800 @8 ft/s
TC ESD (J) - 50%	0.52
TC confined ESD (J)	1
SBAT onset (°F)	434
TC impact (inches) - 50%	>46
TC friction (lbs) - 50%	>64
Russian DDT	no go @ 500 psi
IHE card gap (0 cards)	no go
Characterization	
DSC onset (°C) - 20°C/min	334
VTS (ml of gas/gm) - 100°C, 48 hrs	5.87
H _c (cal/g)	3,222
ΔH _f (kcal/mol; calc)	+119.4
density (g/mL)	1.728

The parameters for the safety testing and characterization are given in Table 2.

The oxidation of DAAOF with ammonium persulfate and hydrogen peroxide in concentrated sulfuric acid gives DNAF in 60% yield.⁵ Attempts to duplicate this result were hindered by the large amount of gassing observed when employing ammonium persulfate. Replacement of this oxidant with sodium persulfate resulted in 50-60% isolated yields of product with much less foaming and off-gassing observed. This work provided samples for initial safety testing and characterization, including a heat of combustion measurement (see Table 5). On first inspection, the very large heat of formation ($\Delta H_f = +185$ kcal/mol), calculated from the heat of combustion test, in combination with the known X-ray crystal density ($\rho = 1.91$ g/cc)²¹, make DNAF a very attractive material for further study. However, the subsequent safety data obtained indicated that the friction and thermal properties of DNAF were not suitable for propellant formulation studies. In addition, the amount of gassing observed during the VTS test was unacceptable for a standard propellant ingredient.

It was postulated that the deficiencies of DNAF may be a result of residual acid or oxidant present from the reagents employed during synthesis. To test this hypothesis, several different purification methods were examined. In the first multiple recrystallizations of DNAF were performed. For the second method, samples of DNAF were dissolved in dichloromethane, the resulting solution washed with aqueous sodium bicarbonate, dried over sodium sulfate, and the solvent evaporated. Then two different recrystallization methods were then employed to give larger (>200-micron) and smaller (<50-micron) crystals of these purified samples. Finally, a simpler process of purification was employed in that the crude DNAF obtained from the final step synthetic step was washed with aqueous sodium bicarbonate and then dried (no recrystallization step). The materials obtained from these experiments were then submitted for safety testing and thermal analysis. The results, along with previous data obtained, are presented in Table 6.

Table 5. Initial Safety Testing and Characterization of DNAF

Test	Result
Safety Testing	
ABL impact (cm) - TIL	6.9
ABL friction (psi) - TIL	50 @ 2 ft/s
TC ESD (J) - 50%	7.75
TC confined ESD (J)	1.00
SBAT onset (°F)	170
TC impact (inches) - 50%	15.0
TC friction (lbs) - 50%	13.0
Characterization	
DSC onset (°C) - 20°C/min	262
VTS (ml of gas/gm) -100°C, 48 hrs	7.8
%C (%C theoretical)	18.13 (17.66)
%H (%H theoretical)	0.00 (0.00)
%N (%N theoretical)	40.83 (41.18)
H _c (cal/g)	2,064
ΔH _f (kcal/mol; calc)	+185.3

The parameters for the safety testing and characterization are given in Table 2.

Table 6. Safety Properties of DNAF

Properties	Impact (cm)	Friction (psi)	ESD (J)	SBAT onset (°F)
Baseline	6.9	50 @ 2ft/s	7.75	170
Multiple recrystallizations, <50 micron	3.5	25 @ 3ft/s	1.05	253
Washed with bicarb, >200 micron	13	100 @ 3ft/s	>8	277
Crude product, washed with bicarb, >50 and <200 micron	3.5	50 @ 4ft/s	0.71	134

The parameters for the safety testing and characterization are given in Table 2.

The more involved purification process of washing solutions of DNAF with aqueous bicarbonate improved the thermal and safety properties of DNAF (larger crystal size) compared to previous results. In addition, the volume of gas observed during VTS testing was lowered, but still substantial (5.5 ml of gas/gram). However, the smaller crystals were still unsuitable for further studies. The simpler purification process on crude DNAF yielded material which was unsuitable, especially in terms of thermal stability. Compatibility testing of DNAF with a set of standard propellant ingredients was performed using DSC analysis. The ingredients included the curatives isophorone diisocyanate (IPDI) and Desmodur N-100, the hydroxy-terminated polybutadiene binder R-45M, aluminum powder, and the bonding agent HX-752. The results are presented in Table 7. The only ingredient which was compatible with DNAF was aluminum powder. This information also indicates that DNAF, in its present form, is not a suitable propellant ingredient.

Table 7. DSC Compatibility Testing of DNAF

Compound	Baseline Departure (°C)	ΔBaseline Departure (°C)	Onset (°C)	ΔOnset (°C)
DNAF	219	-	251	-
IPDI	177	-	-	-
N-100	279	-	-	-
R45M	206	-	-	-
Al	-	-	-	-
HX-752	159	-	181	-
DNAF/IPDI	89	88	221	30
DNAF/N-100	97	182	152	99
DNAF/R-45M	102	104	127	124
DNAF/Al	217	2	250	1
DNAF/HX-752	83	76	112	139

Another oxidation product from DAF is ANF. A recently developed synthesis of this material utilizes sodium tungstate dihydrate, methanesulfonic acid and hydrogen peroxide to oxidize DAF and gives 60-65% yields of ANF.⁶ This procedure was employed to produce multi-gram samples of ANF. Multiple recrystallizations from ethyl acetate or water gave high purity material for safety testing and characterization. The results are presented in Table 8. Even after exhaustive purification, samples of ANF still showed unacceptably low thermal decomposition temperatures and high levels of off-gassing during thermal aging. These characteristics severely limit the propellant application of this ingredient.

Table 8. Safety Testing and Characterization of ANF

Test	Result
Safety Testing	
ABL impact (cm) - TIL	11
ABL friction (psi) - TIL	800 @8 ft/s
TC ESD (J) - 50%	1.9
TC confined ESD (J)	1
SBAT onset (°F)	213
TC impact (inches) - 50%	42
TC friction (lbs) - 50%	>64
Characterization	
DSC onset (°C) - 20°C/min	200
VTS (ml of gas/gm) - 100°C, 48 hrs	>10
H _c (cal/g)	2,233
ΔH _f (kcal/mol; calc)	+34.2

The parameters for the safety testing and characterization are given in Table 2.

Another furazan-based material investigated was PIPER. This material had been a target in the U.S. for a number of years and had not been synthesized when these studies were initiated.⁷ The initial route attempted is presented in Figure 2. The first three steps are based on a literature procedure.⁸ The last two projected steps are known to give high yields on similar substituted benzyl amines. Unfortunately, the dibenzyl material obtained after the third step proved to be

unreactive toward several standard hydrogenolysis methods. In addition, attempts to remove the benzyl groups with nitrosonium tetrafluoroborate in sulfone resulted in partial nitration of the phenyl rings. Finally, attempted oxidation of the benzyl groups to benzoyl groups with either N-bromosuccinimide/benzoyl peroxide in chloroform or silver pyridinium persulfate ($\text{Ag}(\text{pyr})_4\text{S}_2\text{O}_8$)⁹ were also unsuccessful. Due to the apparent unreactive nature of this precursor an alternate route was investigated. This alternate route is presented in Figure 3. This route held promise in that the very stable (and unreactive) dibenzyl precursor is avoided.

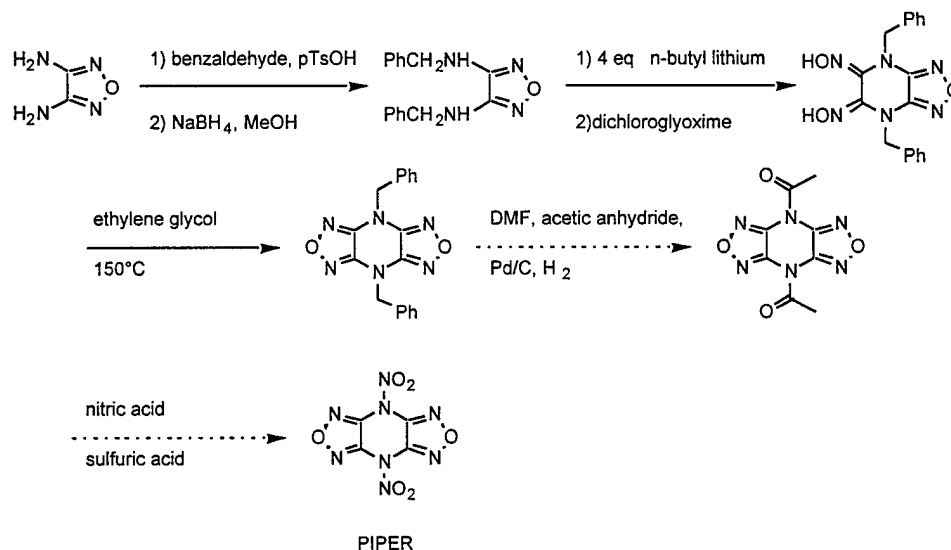


Figure 2. Initial Route Investigated for the Synthesis of PIPER

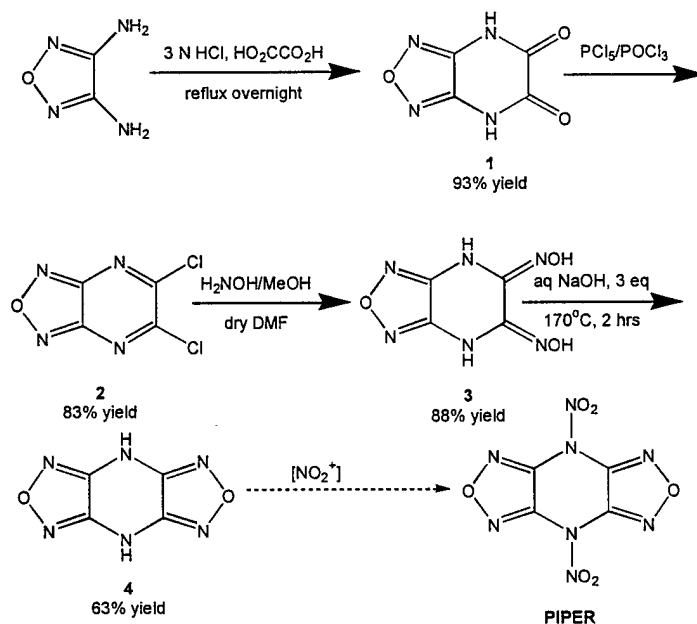


Figure 3. Alternate Route for the Synthesis of PIPER

The conversion of DAF into the oxamide derivative **1** was accomplished by refluxing overnight with one equivalent of oxalic acid in 3M hydrochloric acid. The isolated yield of **1** was 93%. The oxamide derivative **1** was then converted into the dichloride derivative **2** using a mixture of phosphorus pentachloride (PCl_5) and phosphorus oxychloride (POCl_3). After bringing to reflux for 2 hours, the clear solution was evaporated to remove the original POCl_3 and the POCl_3 produced during the reaction. The crude product was recrystallized from dry ethyl acetate to afford the dichloride **2** in >90% isolated yield. In the next step the dichloride **2** was allowed to react with neat hydroxylamine in dry dimethylformamide (DMF) with cooling. An excess of hydroxylamine was employed to neutralize the hydrochloric acid that is produced. The resulting hydroxylamine hydrochloride was filtered off, the filtrate was diluted with water, and the product bis oxime **3** was isolated by a filtration. The crude product (obtained in quantitative yield) was washed with copious amounts of water and recrystallized from hot DMF. The purified bis oxime **3** was heated in dry DMF at 170°C in a sealed tube for 4 hours which cleanly converted **3** into the bis furazan **4** (as determined by ^{13}C NMR analysis of the reaction when performed in d_6 -DMF). However, isolation of the product from the DMF proved to be very difficult and often resulted in partial or complete decomposition of the desired material. In addition, it was observed that impurities present in **3** will lead to formation of side products during the synthesis of **4**. Other solvents besides DMF were examined for the conversion of **3** into **4**. Pyridine (at 110°C overnight) gave no reaction. Employing dimethyl sulfoxide (DMSO) (at 180°C) led to decomposition. Toluene at 170°C overnight gave only starting material. Nitrobenzene cleanly gave product at 170°C, but the solubility of **3** was so low that large amounts of solvent were required. The classic method of dehydrating glyoximes, using potassium hydroxide in water at 150-170°C in a sealed autoclave, to give furazans was also investigated. Isolated yields of product were eventually improved to 63% after optimization of the workup conditions. This method was used to prepare several multi gram batches of material.

The last step in the synthesis of PIPER is the nitration of the bis furazan **4**. Initial attempts on the nitration, using nitronium tetrafluoroborate, either yielded only starting material under less forcing conditions or led to decomposition of **4** when higher temperatures and larger amounts of nitrating agent are employed. This nitration was attempted with 100% nitric acid, acetyl nitrate, nitrogen pentoxide (N_2O_5), nitronium tetrafluoroborate (NO_2BF_4), and mixed acid. Identification of products was difficult since PIPER has no protons and one carbon environment surrounded by nitrogens in the desired product. Nitration with acetyl nitrate gave the diacetate and not the nitrated product. This was identified by NMR and elemental analysis. Reaction of the bis furazan **4** with the strong bases sodium hydroxide (NaOH) or potassium hydroxide (KOH) gives the corresponding dibasic salt. Attempted nitration of this salt in protic media returns the amine (protonation occurs faster than nitration), so nitration was attempted in anhydrous aprotic conditions. Nitration with N_2O_5 in organic solvents gives a mixture of products that may include PIPER under some conditions (evidence for this is from the nitro group peaks and lack of N-H stretches in the IR). Other products appear to include the oxidation product of the anion, the piperazine diradical. This product, which is stable as a solid at room temperature, is soluble in, but reactive with, most solvents, giving highly colored solutions. It has no proton NMR resonances and one ^{13}C NMR resonance. It can be initiated by impact.

Based on the results obtained on the nitration of **4** to give PIPER, it appears that PIPER is not a viable material for solid propellant applications. These results are in agreement with an independent successful synthesis of the compound presumed to be PIPER.⁷ It is disappointing that this compound, which appears so attractive on paper, is not a viable material.

The reported synthesis of TATFO is presented in Figure 4.¹⁰ Diaminofurazan (DAF), the product from completing the first two steps of the synthesis, was synthesized as described previously. This material was allowed to react with lead tetraacetate in acetonitrile to give a 33% isolated yield of tetrazotetrafurazan (TATF). Flash chromatography using silica gel was required in order to separate the desired product from other cyclic oligomers formed during the reaction. The next step was performed by dissolving TATF in concentrated sulfuric acid and treating the resulting solution with 30% hydrogen peroxide at room temperature for 6 hours. The crude product precipitated from the reaction mixture and was further purified using flash chromatography on silica gel. An 45% yield of TATFO was obtained by the process. The yields obtained in both steps were significantly below that reported in the literature.

Samples of purified TATFO were submitted for small scale safety properties and the data is given in Table 9. These values indicate extreme impact and friction sensitivity. However, the thermal stability was excellent, as was found with all of the furazan-based materials. In an attempt to improve the safety properties of TATFO, multiple purifications using silica gel chromatography were employed. This was unsuccessful in yielding material which had improved safety properties. It was hoped that some of the impurities present were giving the unwanted sensitivity, but this does not appear to be the case.

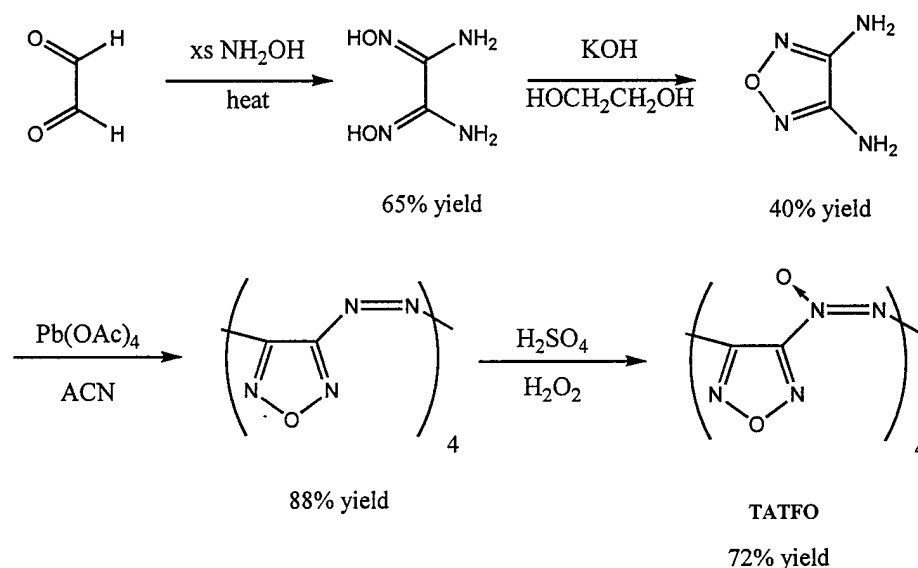


Figure 4. Synthesis of TATFO

Table 9. Safety Testing of TATFO

Test	TATFO	acceptable limit
ABL impact (cm) - TIL	<1.1	≥3.5
ABL friction (psi) - TIL	25 (2 ft/s)	≥50 (3 ft/s)
TC ESD (joules) - 50%	0.18 (mass ignition)	no mass ignition
TC confined ESD (j)	0.125	N/A
SBAT onset (°F)	325	>225°F
TC impact (inches) - 50%	40.80	>4
TC friction (lbs) - 50%	13.50	>10

CONCLUSIONS

In summarizing the program's investigation of furazan-based energetic materials, it was found that only one compound, DAAOF, had acceptable thermal and compatibility properties for solid propellant applications. It appears that attaching amino and nitro functional groups to the furazan ring (e.g. ANF, DNAF, PIPER) adversely impacts the thermal stability and compatibility properties of these materials. Future basic research on furazans needs to be directed toward understanding the chemical mechanism behind these observations. Narrowing the list of candidate furazans for future evaluation to those which do not contain these groups is recommended.

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